DECOMPOSITION OF NITRONIUM PERCHLORATE*

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Abstract

The decomposition reaction for nitronium perchlorate is believed to be the formation of nitrosonium perchlorate and oxygen. The other products (NO_2, Cl_2, ClO_2) observed during the decomposition appear to be the result of the subsequent decomposition of nitrosonium perchlorate. This mechanism is clearly demonstrated *in vacuo* by a preponderance of oxygen in the volatiles during the early stages of the decomposition of nitronium perchlorate and by the products of the latter stages which describe the decomposition of nitrosonium perchlorate.

In sealed tubes, the reaction of dinitrogen tetroxide with nitronium perchlorate ultimately predominates, giving nitrosonium perchlorate and oxygen as products. This reaction has been shown to be catalyzed by dinitrogen tetroxide.

Introduction

Nitronium perchlorate begins to decompose slowly at approximately 50°C resulting in the production of gaseous products. There is some evidence that the purity of the sample is related to the decomposition. On the other hand, despite efforts by several investigators to obtain high-purity samples, decomposition is significant by 60°C.

Our interest in this problem was one of establishing the mechanism for the decomposition. By doing so we hoped to obtain information that would allow us to prevent or suppress the decomposition.

The decomposition of nitronium perchlorate between 70 and 112°C has been reported by Cordes[1] as proceeding to the gaseous products: NO_2, Cl_2, ClO_2, NO_3Cl and O_2. As a result of some screening experiments at Callery we were aware that, at 65°C in sealed tubes, nitrosonium perchlorate was a major decomposition product. We were also aware that dinitrogen tetroxide, at least in the liquid phase, would quantitatively convert nitronium perchlorate to nitrosonium perchlorate. Thus, a mechanism involving only gaseous products appeared unlikely.

To avoid any such back reaction of dinitrogen tetroxide with nitronium perchlorate we decided to carry out our study under vacuum, with continuous removal of products. The temperature of 65°C was chosen so as to give a significant decomposition rate, but one at which the gaseous products could be handled by the pumping system.

Experimental

The decompositions were carried out in glass reactors connected through a short coupling to a small vacuum system. Nitronium perchlorate is extremely hygroscopic, and even with utmost care, the presence of hydrolysis products cannot be avoided. Therefore, after completing the sample transfer to the decomposition

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(1) Cordes, H. F., J. Phys. Chem. 67, 1693 (1963).

reactor, the removal of hydrolysis products (HNO_3 and $HClO_4$) were effected by pumping at 10^{-5} mm of mercury at room temperature until a constant weight was obtained.*

The decomposition was monitored at 65°C while continuously pumping on the sample. A pressure of at least 10^{-4} mm of mercury was maintained in the system. The volatile decomposition products were passed through a -196°C trap, where condensables were removed and periodically analyzed. Non-condensables, consisting entirely of oxygen, were Toeplerized either continuously, or periodically to check their rate of removal. The weight-loss of the sample was checked against volatiles recovered or measured and appropriate analyses carried out on the residue. Sublimed nitronium perchlorate was weighed with the residue. On most runs, the sublimed solids were measured and analyzed.

Results and Discussion

The decomposition experiments were characterized by: (1) An immediate deposition of sublimed materials on the cooled reactor walls within one minute after placing the sample in the 65°C bath; (2) An induction period of 24-40 hours during which no visible evidence of volatiles was observed; (3) An initially slow, but rapidly accelerating production of oxygen which maximized at approximately 100 hours with concurrent appearance of yellow condensable in the -196°C trap; and finally (4) A noticeable decrease in the rate of oxygen evolution which diminished slowly throughout the remainder of the run.

Oxygen Evolution

A plot of the total oxygen evolved versus time gave the typical sigmoid curve characteristic of solid decomposition (Figure 1). The induction and acceleration periods are clearly evident, along with the subsequent lower rate of total oxygen evolution during the decay stage.

A plot of the rate of oxygen evolution for one experiment is shown in Figure 1. The peak rate of oxygen release occurred at approximately 100 hours, at about a 10% weight loss, and with more than 80% of the nitronium perchlorate still intact in the sample (80% figure obtained from a similar run stopped at this point and the solids analyzed.).

The ratio of oxygen released per gram of weight-loss incurred also varied throughout the run. Table I summarizes this data for two experiments.

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* The effectiveness of this procedure was demonstrated by adding a measured amount of water to a sample of nitronium perchlorate and, after pumping according to the procedure described, the weight-loss was measured for the sample and the nitric and perchloric acids titrated in the recovered volatiles. All values were theoretical within limits of the analyses.

TABLE I

RATIO OF OXYGEN EVOLVED PER GRAM WEIGHT-LOSS

Total Time (hrs.)	Wt. Loss (g)	O_2 (mmoles)	mmoles O_2 / g. wt. loss
Run No. 1			
29	-----	0.02	----
73	0.160	2.46	15.5
92	0.140	2.01	14.3
112	0.161	2.13	13.3
132	0.154	1.93	12.6
154	0.163	1.80	11.1
174	0.150	1.47	9.8
Run No. 2			
198	0.341	3.98	11.7
298	0.177	1.32	7.3
397	0.129	0.88	6.8
492	0.103	0.66	6.5

The change from 15.5 to 6.5 for the mmoles of O_2 per gram wt.-loss is significant in that it denotes a mechanism change, or the increasing importance of a secondary reaction. The 15.5 and 6.5 values are also significant since they cannot be obtained from nitronium perchlorate decomposition reactions giving only gaseous products, but they must arise from a combination of reactions in which the production and decomposition of $NOClO_4$ is involved. The highest and lowest possible values obtainable from NO_2ClO_4 for this ratio are shown by the equations

	(mmoles O_2/g. wt. loss)
$NO_2ClO_4 \longrightarrow NO_2 + 1/2\ Cl_2 + 2\ O_2$	13.8
$NO_2ClO_4 \longrightarrow NO_2 + ClO_2 + 1/2\ O_2$	6.9

On the other hand, values of 31.3 and 3.9 are possible from the production and decomposition, respectively, of nitrosonium perchlorate.

	(mmoles O_2/g. wt. loss)
$NO_2ClO_4 \longrightarrow NOClO_4 + 1/2\ O_2$	31.3
$NOClO_4 \longrightarrow NO_2 + ClO_2 + 1/2\ O_2$	3.9

Volatiles Condensable at -196°C

The condensed materials were identified as NO_2, Cl_2 and ClO_2 by means of infrared and mass spec. analyses. The sample was hydrolyzed and analyzed for chlorine and nitrogen content. The combined equivalents of chlorine (Cl_2 + ClO_2) invariably equaled the equivalents of nitrogen found, within limits of the analyses.

The nitrogen dioxide produced (measured as nitrogen in the hydrolysate) per gram of weight-loss of sample slowly increased as the decomposition progressed. The values for two runs are shown in Table II.

TABLE II

NO_2 PRODUCED PER GRAM OF WEIGHT-LOSS

Total Time (hrs.)	Wt. Loss (g)	NO_2 Produced (mats)	mmoles NO_2 / g. wt. loss
Run No. 1			
73	0.160	0.90	5.6
92	0.140	0.77	5.5
112	0.161	0.93	5.8
132	0.154	0.99	6.4
154	0.163	1.07	6.6
174	0.150	1.02	6.8
Run No. 2			
397	0.647	4.32	6.7
492	0.103	0.78	7.6

It is again significant that the value of 7.6 mmoles of NO_2 per gram of weight-loss of sample obtained over the last period from 397 to 492 hours of decomposition for Run No. 2 cannot be obtained from any decomposition reaction one may write for NO_2ClO_4. It is, however, nearly theoretical for the decomposition of $NOClO_4$ to volatiles.*

	mmoles NO_2 / g. wt. loss
$NOClO_4 \longrightarrow NO_2 + ClO_2 (Cl_2 + 1/2\ O_2$	7.7

Analysis of Solids

In our original hypothesis, we believed the formation of $NOClO_4$ in the residue would be avoided by carrying out the decomposition under vacuum. By doing so, we hoped to prevent the back reaction of the NO_2 produced in the decomposition with NO_2ClO_4. Nevertheless, $NOClO_4$ was observed in the residue in substantial quantities, possibly suggesting its formation by a different mechanism. Its presence was confirmed by x-ray, Raman and wet analysis techniques.

Figure 2 compares the $NOClO_4$ found in the residue with the NO_2ClO_4 decomposed as a function of time. With the limited data available, the peak production of $NOClO_4$ is observed to coincide with the peak rate of NO_2ClO_4 decomposition. The $NOClO_4$ also appears to decompose at a faster rate than the nitronium perchlorate as indicated by the slopes of the curves. This would most certainly be true if, as we suspect, nitrosonium perchlorate is also being continuously produced from the decomposition of nitronium perchlorate during this period.

A study of the decomposition of $NOClO_4$ under conditions identical to this study gave the following results: (1) Nitrosonium perchlorate decomposes with no noticeable induction period, giving only the gaseous products, NO_2, ClO_2, Cl_2 and O_2; nitronium perchlorate is reported as a major product of this decomposition at 99°C(2) but only trace quantities were observed in our study. (2) The decomposition

* A value of 7.6 mmoles of NO_2 per gram of weight loss was observed experimentally for the decomposition of $NOClO_4$ under similar conditions.

(2) Rosolovskii, V. Ya, and Rumyantsev, E. S., Russ. J. of Inorg. Chem., English Transl. 8, 689 (1963).

of $NOClO_4$ proceeds at a faster rate than that for NO_2ClO_4, at least after the acceleratory period of the latter compound. This observation is consistent with conclusions of Rosolovskii[2].

Several interesting facts concerning the sublimed solids should be noted: (1) Sublimation occurred immediately upon heating the sample to 65°C; (2) The sublimed solids analyzed to be NO_2ClO_4 both by x-ray and elemental analyses; (3) Analyses did not detect the presence of $NOClO_4$; (4) The rate of sublimation appeared to be comparatively constant over the decomposition period; sublimation usually occurred at about 1/2 to 1/3 the rate of decomposition. These facts are significant in that they indicate the sublimation to be entirely independent of the decomposition.

The Decomposition Mechanism

The vacuum decomposition of NO_2ClO_4 at 65°C proceeds by a mechanism which must take into account: (1) A decreasing ratio of oxygen evolution per weight-loss of sample; (2) An increasing ratio of NO_2 production per weight-loss of sample; (3) The production of $NOClO_4$ as a product and its subsequent decomposition, and (4) The decomposition of $NOClO_4$ as the predominant reaction in the latter stages. The observations are best explained by the following two-step mechanism:

(a) $NO_2ClO_4 \longrightarrow NOClO_4 + 1/2\ O_2$

(b) $NOClO_4 \longrightarrow NO_2 + ClO_2\ (Cl_2 + O_2) + 1/2\ O_2$

Assuming the mechanism as described, the ratios of O_2 and NO_2 per gram of weight-loss expected from equations (a) and (b) in various ratios can be calculated. These are tabulated in Table III.

TABLE III

CALCULATED QUANTITIES OF O_2 AND NO_2 PRODUCED PER WEIGHT LOSS OF NO_2ClO_4

Ratio Equations a:b	mmole produced/g. wt.-loss NO_2	O_2, Assuming all Cl as ClO_2	O_2, Assuming all Cl as Cl_2
10:0	none	31.2	31.2
10:1	3.5	19.0	22.5
10:2	4.8	14.4	19.1
10:3	5.5	11.8	17.3
10:4	5.8	10:3	16.2
10:6	6.4	8.5	14.9
10:8	6.7	7.5	14.2
10:10	6.9	6.9	13.8
8:10	7.0	6.3	13.4
6:10	7.2	5.8	12.9
4:10	7.4	5.2	12.5
2:10	7.5	4.5	12.1
0:10	7.7	3.9	11.6

The NO_2 and O_2 values thus lie between the extremes of none and 31.2 for the initial stage which describes the production of $NOClO_4$; and 7.7 and 3.9 to 11.6 for the latter stage which describes the decomposition of $NOClO_4$.

The experimental values for these same ratios for the two experiments previously cited are shown in Table IV.

TABLE IV

EXPERIMENTAL O_2 AND NO_2 WEIGHT-LOSS RATIOS

Total Time (hrs.)	mmoles O_2/g wt. loss	mmoles NO_2/g wt. loss
Run No. 1		
73	15.5	5.6
92	14.3	5.5
112	13.3	5.8
132	12.6	6.4
154	11.1	6.6
174	9.8	6.8
Run No. 2		
198	11.7	
298	7.3	6.7
397	6.8	
492	6.5	7.6

The general trends for the mmoles of O_2 and NO_2 produced per weight-loss are observed to follow those expected for the proposed mechanism. That reaction (a) predominates in the early stages is supported by the initially high experimental values obtained for the ratio of O_2 evolution per weight-loss of sample. A theoretical value of 31.3 would be expected if only (a) occurred, since oxygen is the only volatile. This would be true only momentarily, since $NOClO_4$ decomposes rapidly at 65°C without any induction period by equation (b) which would immediately become operative. Any contribution by (b) would lower the oxygen to weight-loss ratio, since at its highest possible rate of oxygen production, (giving NO_2, Cl_2 and O_2 as decomposition products), a theoretical 11.6 value for the ratio of mmoles of oxygen to weight-loss would be observed. The initial value of 15.5 observed after 73 hours is therefore a "net" figure for reactions (a) and (b) during this initial interval, and represents a substantial contribution from reaction (a).

A quantitative correlation of equations (a) and (b) with the oxygen ratio is not possible because of the uncertainty in the quantity of ClO_2 decomposed to Cl_2 and O_2. On the other hand, the ratio of NO_2 produced per weight-loss can be directly correlated. The initial ratio of 5.6 for NO_2, for example, indicates that, during the first 73 hours, the ratio of equation a:b averaged 10:3, or stated otherwise, approximately 30% of the $NOClO_4$ that was produced during this period by equation (a) subsequently decomposed.

At the finish of Run No. 1, during the interval of 154 to 174 hours, reactions (a) and (b) were operating at an approximate 10:9 ratio. Thus, $NOClO_4$ decomposed at nearly the same rate as its production from NO_2ClO_4.

The 7.6 value for the NO_2 ratio, obtained over the period of 397 to 492 hours of Run No. 2 indicates that the decomposition of $NOClO_4$ (equation b) was occurring ten times faster than it was being produced from equation (a), thus rapidly diminishing the excess produced during the accelerated period of the NO_2ClO_4 decomposition.

The 7.6 value for NO_2 production and the 6.5 value for the oxygen evolution obtained in the latter stages of the decomposition of NO_2ClO_4 are almost

identical to similar values obtained from the decomposition of $NOClO_4$ under similar conditions. The respective values for $NOClO_4$ were 7.6 and 6.9 mmoles per gram of weight-loss, indicating the predominance of this reaction in the latter stages of the NO_2ClO_4 decomposition.

As a further check on this mechanism, the decomposition of NO_2ClO_4 was monitored, using a Raman cell as a decomposition reactor. The changes in the Raman spectrum were measured periodically and compared with the production of oxygen throughout the course of the decomposition at 65°C. The rapid drop in the NO_2^+ absorption by NO_2ClO_4 coincides with the appearance and increase in the NO^+ absorption for $NOClO_4$ (Figure 3), as would be expected from the proposed mechanism. Only the NO_2^+ (1400 cm^{-1}) and NO^+ (2300 cm^{-1}) curves were plotted since the respective perchlorate absorptions closely parallel the cation absorption curves. The oxygen curves are similar to those previously observed (Figure 4). As before, the peak rate of oxygen evolution occurred at approximately 100 hours.

It is significant to note that the Raman data also indicates a break at about 100 hours in the absorption curves for NO_2^+, which was decreasing, and NO^+, which was increasing. Since a Raman spectrum of solids is predominantly a surface phenomenon, this agreement suggests an initially rapid surface reaction converting the surface NO_2ClO_4 to $NOClO_4$ which then controls continued decomposition.

A mechanism for the decomposition of NO_2ClO_4 in the presence of its decomposition products would have the dinitrogen tetroxide-catalyzed conversion of NO_2ClO_4 to $NOClO_4$ in addition to the reactions (a) and (b).

$$NO_2ClO_4 + N_2O_4 \longrightarrow NOClO_4 + N_2O_5$$

$$N_2O_5 \longrightarrow N_2O_4 + 1/2\ O_2$$

When a critical concentration of NO_2 has been reached from the decomposition of nitrosonium perchlorate, this catalytic conversion rapidly becomes the predominating reaction in the mechanism. Previous work at Callery had shown this reaction to be quantitative in the presence of liquid N_2O_4.(3) In the course of this investigation, gaseous N_2O_4 at ambient temperature, in less than equimolar quantities, was also demonstrated to effect the quantitative conversion presumably by the above mechanism.(3)

Discussion of Thermal Stability

The foregoing discussion does not explain the reasons for the instability of NO_2ClO_4, but with this information a reasonable picture as to the decomposition process can be presented.

Borrowing from the classical concept of solid decompositions, decomposition probably initiates at defect sites on the crystal surface where circumstances offer a lowered energy of activation.(4) It appears most probable that the decomposition initiates with $NOClO_4$ formation. Therefore, ion interactions are involved.

It can be stated that the instability of NO_2ClO_4 is not inherent in the nitronium ion. More stable nitronium species are known; NO_2BF_4 is reportedly

(3) A. D. McElroy and M. D. Marshall; to be published.
(4) Garner, "Chemistry of the Solid State" Butterworth Scientific Publications, London, (1955), Ch. 7.

stable at 170°C[5], and $(NO_2)_3Al(ClO_4)_6$ and $NO_2Zn(ClO_4)_3$ are quantitatively prepared at 125°C[6], a temperature at which NO_2ClO_4 rapidly decomposes. We are also well aware of stable perchlorate salts. Obviously, then the instability of NO_2ClO_4 is peculiar to the NO_2^+ and ClO_4^- ion combination.

The following mechanism is suggested as occurring at the crystal surface.

$$NO_2^+ + ClO_4^- \rightleftharpoons [NO_2ClO_4] \begin{cases} \rightarrow NO_2ClO_4(\text{sublimed}) \\ \rightarrow NOClO_4 + 1/2\ O_2 \end{cases}$$

Nitronium perchlorate, as an ion-complex may exist as a transitory intermediate which may either revert to ions, sublime or decompose. A similar mechanism has been proposed for the decomposition of ammonium perchlorate[7].

Evidence for interaction between the NO_2^+ and ClO_4^- ions has been observed in the NO_2ClO_4 crystal lattice. Distortions from linearity in the NO_2^+ ion, and from the tetrahedral angle for the Cl-O bonds of the ClO_4^- have been interpreted by Truter et al., as due to interaction between cation and anion[8]. In addition, both Raman and infrared spectra of nitronium perchlorate obtained here at Callery have shown the splitting of the perchlorate Cl-O bands which, according to Hathaway[9], is characteristic of bidentate coordination for the perchlorate group. Thus, something less than a truly ionic crystal lattice is present in NO_2ClO_4 and decomposition may therefore be facilitated by this interaction.

In complex perchlorates [e.g. $(NO_2)_3Al(ClO_4)_6$, $(NO_2)Zn(ClO_4)_3$], the ClO_4^- ion is coordinated by the aluminum or zinc ions and therefore has little tendency to interact with the NO_2^+ ion. In NO_2BF_4, the BF_4^- ion presumably exerts very little distorting influence. Thus, in these compounds, the ionic distortion of the NO_2^+ is minimized and an increased thermal stability results.

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(5) Kuhn and Olah, JACS 83, 4565-71 (1961).
(6) McElroy, A. D., Guibert, C. R., Bellissimo, J. S., and Hashman, J. S., J. Inorg. Chem., to be published; presented Gordon Research Conference, August, 1963.
(7) Galwey, A. K. and Jacobs, P. W. M., Proc. of Royal Chem. Soc., Series A, 254, 455 (1960).
(8) Truter, M. R., Cruikshank, D. W. J., and Jeffrey, G. A., Acta Cryst. 13 855 (1960).
(9) Hathaway, B. M., and Underhill, A. E., J. Chem. Soc., 3091 (1961).

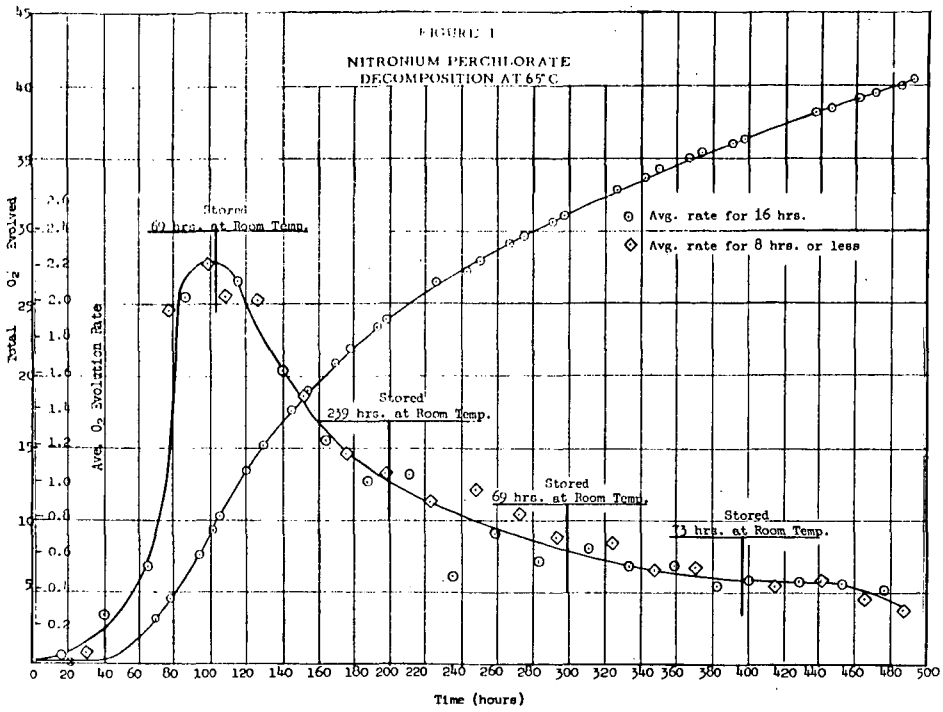

FIGURE 2

DECOMPOSITION OF NO_2ClO_4 AT 65°C

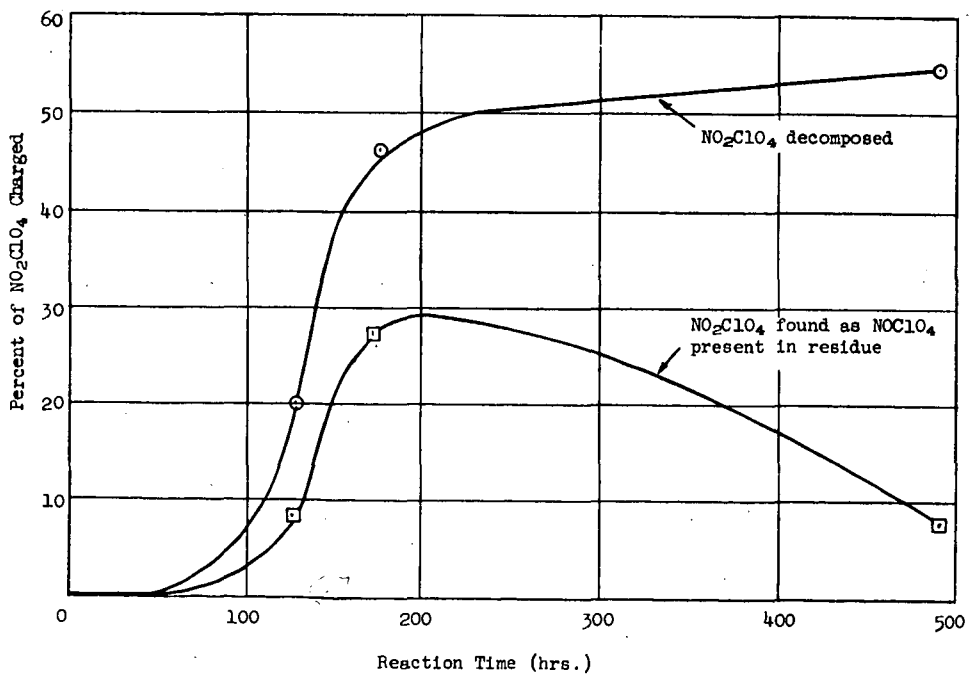

FIGURE 3

RAMAN ANALYSIS OF DECOMPOSITION OF NO_2ClO_4 at 65°C

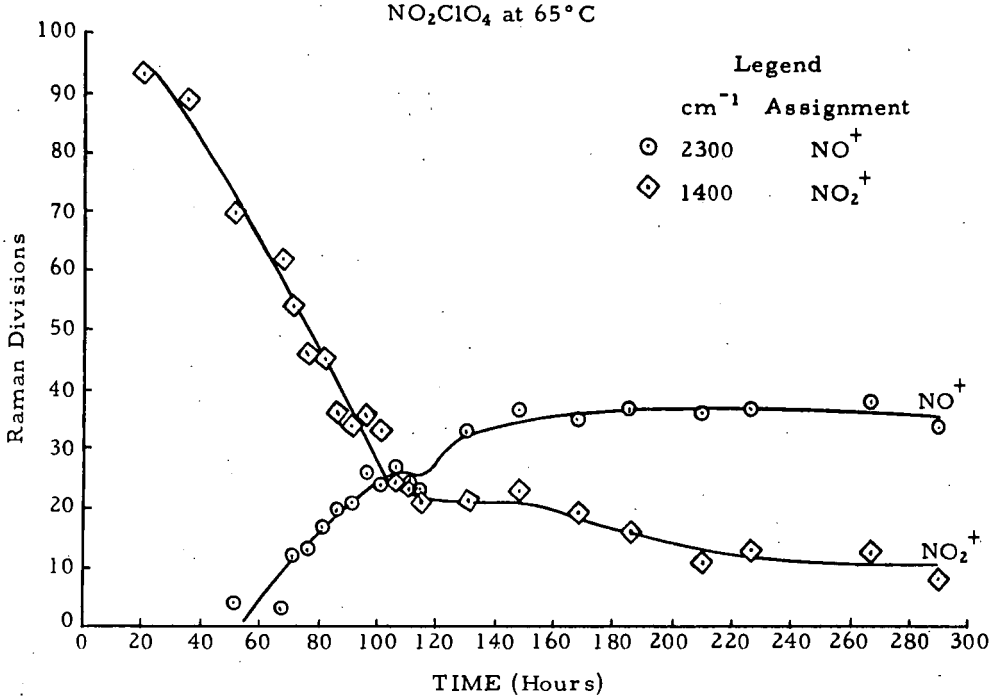

FIGURE 4